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Synthesis of Multiple Hydrogen-Bonded Unit Containing Polymer *via* Acyclic Diene Metathesis (ADMET) Polymerization of Oligoamide Monomer with Grubbs-Type Olefin Metathesis Catalysts

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The multiple hydrogen-bonded unit containing polymer was synthesized by using acyclic diene metathesis polymerization of oligoamide monomer with Grubbs-type olefin metathesis catalysts. The polymer was characterized by nuclear magnetic resonance, gel permeation chromatography and scanning electron microscope. The results demonstrate the successful synthesis of novel polymer *via* acyclic diene metathesis polymerization and the hydrogen-bonding-assisted formation of aggregates.

Keywords: Multiple hydrogen-bonded unit, Oligoamide, Functional polymer, Acyclic diene metathesis polymerization.

INTRODUCTION

Acyclic diene metathesis (ADMET) polymerization is a relatively new route to novel organic polymers that has been explored by Wagener *et al.*[1,2] and made possible by the highly selective catalysts developed by Grubbs and Schrock[3,4]. Among various polymerization techniques that can be used to obtain target polymers, acyclic diene metathesis polymerization has proven a valuable tool for the construction of new polymer architectures due to the high catalytic activity and its high functional group tolerance. Acyclic diene metathesis chemistry allows the polymerization of many different monomers with a high degree of functionality and produces regular, well-defined, polymers[5]. However, less work in this area has been reported with monomers as large, or as complex, as described in this article. The functionality and bulkiness of the monomers described here illustrate the versatility of the acyclic diene metathesis polymerization route.

Oligoamide molecular strands **1** with the self-complementary hydrogen-bonding sequences ADAD can form a stable (K_a-10^4 M^{-1}) molecular duplex 1·1 in chloroform (Fig. 1)[6,7]. In this paper we describe the use of oligoamide monomer **1** to construct multiple hydrogen-bonded unit containing polymer (MHP) *via* acyclic diene metathesis polymerization with

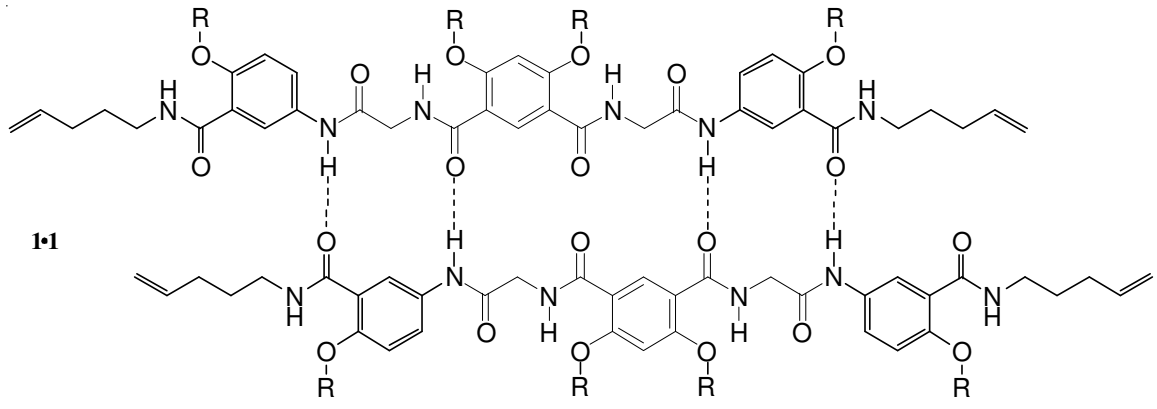


Fig. 1. Oligoamide molecular duplex 1·1 bearing self-complementary hydrogen bonding ADAD sequences

Grubbs-Type olefin metathesis catalysts. The formation of the MHP was investigated by nuclear magnetic resonance (NMR) and gel permeation chromatography (GPC). In addition, the morphology of the hydrogen-bonding-assisted assembled of MHP was examined by scanning electron microscope (SEM).

EXPERIMENTAL

All reactions were conducted with oven-dried glassware under atmosphere or nitrogen. Chemical grade reagents were used without further purification. Solvents were dried and distilled following usual protocols. Column chromatography was carried out using silica gel (300-400 mesh). The ^{1}H and ^{13}C NMR spectra were recorded on Bruker AVANCE AV II-400 MHz (^{1}H: 400 MHz; ^{13}C: 100 MHz) and Bruker Avance AVANCE AV II-600 MHz (^{1}H: 600 MHz; ^{13}C: 150 MHz). Chemical shifts were expressed in parts per million (δ) using tetramethylsilane (TMS) or residual solvent protons as internal standards (^{1}H: chloroform: δ 7.26 ppm; DMSO: δ 2.49 ppm; ^{13}C: $CDCl_3$: 77.23 ppm.). Gel permeation chromatography (GPC) was used to determine the molecular weights and polydispersity indices of the polymers on the basis of a polystyrene calibration curve. The gel permeation chromatography instrument was performed on Waters 150-c ALC/GPC and was equipped with two consecutive Waters Styragel columns (2 × 30 cm) including a RI detector. The scanning electron microscopy (SEM) images were obtained from a JEOL JSM-5900 LV instrument with an acceleration voltage of 20 KV.

General procedure for the synthesis of compounds A and B: Compounds **A** and **B** were prepared according to previously reported literature procedure and compound **A** was used for the next step without isolation and further purification after catalytic hydrogenation[8].

Compound B: White solid (90 % yield). ^{1}H NMR (400 MHz, DMSO-d_6): δ 12.76 (br, 2H), 8.53 (s, 1H), 8.29 (t, *J* = 5.2 Hz, 2H), 6.79 (s, 1H), 4.25 (t, *J* = 6.4 Hz, 4H), 4.02 (d, *J* = 5.2 Hz, 4H), 1.85 (m, 4H), 1.43-1.20 (m, 20H), 0.85 (t, *J* = 6.8 Hz, 6H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 170.88, 163.52, 160.14, 134.87, 113.87, 97.88, 69.44, 41.39, 31.02, 28.49, 28.41, 28.11, 25.33, 21.88, 13.73.

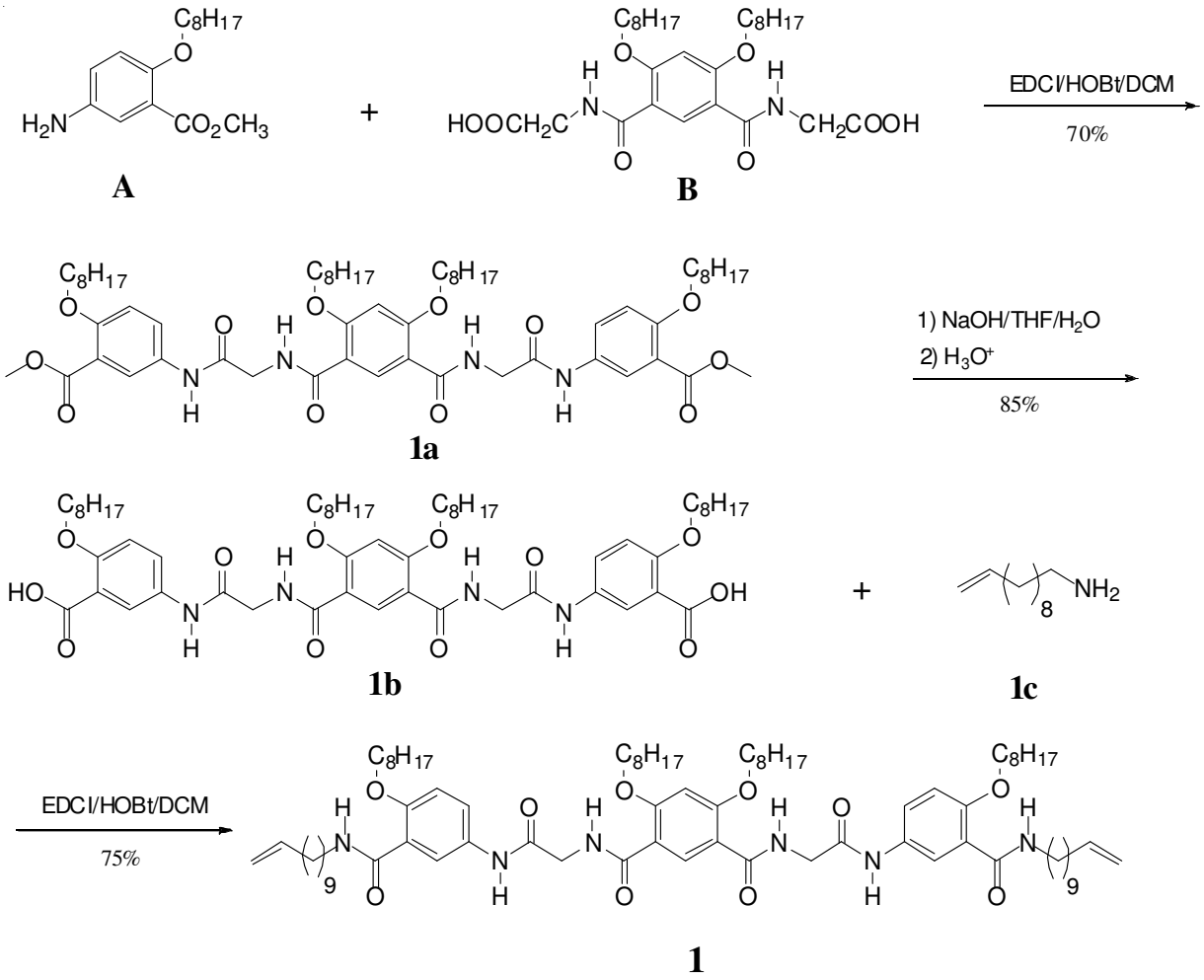
Compound 1a[8]: A mixture of acid B (3.9 g, 7.3 mmol), EDCl (1.7 g, 8.76 mmol) and HOBt (1.2 g, 8.76 mmol) was dissolved in dry CH_2Cl_2 and stirred for 1 h. Then the solution of amide A (4.3 g, 14.5 mmol) in dry CH_2Cl_2 was dropped into the mixture under N_2 atmosphere. After stirring overnight at room temperature, the solvent was removed under reduced pressure. The crude product was further purified by column chromatography (silica, 5 % methanol/chloroform) to give **1a** as white solid (70 % yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.12 (s, 2H), 9.06 (s, 1H), 8.46 (t, *J* = 4.9 Hz, 2H), 7.91 (d, *J* = 2.6 Hz, 2H), 7.85 (dd, *J* = 9.0, 2.6 Hz, 1H), 6.93 (d, *J* = 9.0 Hz, 2H), 6.52 (s, 1H), 4.37 (d, *J* = 4.9 Hz, 4H), 4.09 (d, *J* = 5.5 Hz, 4H), 3.87 (dd, *J* = 5.5, 2.0 Hz, 4H), 3.85 (s, 6H), 1.98 (dt, *J* = 12.0, 6.0 Hz, 2H), 1.73 (dt, *J* = 12.2, 6.0 Hz, 2H), 1.62 - 1.23 (m, 32H), 0.97 (t, *J* = 7.4 Hz, 6H), 0.93-0.85 (m, 18H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.83, 165.01, 164.52, 160.54, 153.22, 136.44, 132.89, 124.95, 123.51, 121.85, 115.33, 112.97, 96.51, 69.91, 69.58, 44.69, 40.13, 31.92, 31.81, 31.62, 29.52, 29.47, 29.41, 29.38, 29.24, 26.86, 26.30, 22.65, 22.61, 14.07, 13.97. *m/z* calcd for $[C_{60}H_{90}N_4O_{12} + H]^+$ 1059.6555; found: 1059.6587.

Compound 1b: Compound **1a** (0.58 g, 0.55 mmol) was dissolved in THF (20 mL), to which a solution of NaOH (0.066 g, 20 mL) in H_2O (20 mL) was added. The mixture was heated under reflux for 30-40 min and water (100 mL) was added. The aqueous layer was neutralized by addition of concentrated HCl to pH 3. The precipitated crude product was collected and recrystallized from MeOH to give **1b** as white solid (93 % yield).

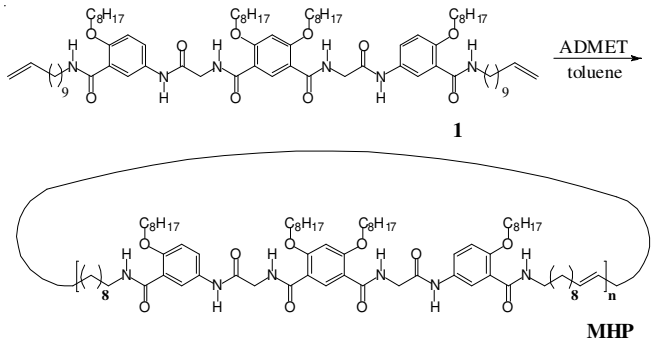
Compound 1c: Compound **1c** was prepared according to previously reported literature procedure[8]. White solid (69.5 % yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.82 (m, 1H), 4.96 (m, 2H), 2.67 (t, 2H), 2.02 (dd, 2H), 1.32 (m, 16H).

Monomer 1 (Scheme-I): A mixture of acid **1b** (0.21 g, 0.2 mmol), EDCl (0.1 g, 0.57 mmol) and HOBt (0.077 g, 0.57 mmol) was dissolved in dry CH_2Cl_2 and stirred for 1 h. Then the solution of **1c** (0.105 g, 0.51 mmol) in dry CH_2Cl_2 was added into the mixture under N_2 atmosphere. After stirring overnight at room temperature, the solvent was removed under reduced pressure. The crude product was further purified by column chromatography (silica, 3 % methanol/chloroform) to give **1** as white solid (70 % yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.88 (s, 2H), 8.92 (s, 1H), 8.36 (s, 2H), 8.20 (dd, *J* = 8.8, 2.0 Hz, 2H), 8.08 (d, *J* = 2.5 Hz, 2H), 8.06 - 8.01 (m, 2H), 6.89 (d, *J* = 9.1 Hz, 2H), 6.44 (s, 1H), 5.73 (ddt, *J* = 17.0, 10.2, 6.7 Hz, 2H), 4.88 (dd, *J* = 23.3, 13.7 Hz, 4H), 4.53 (d, *J* = 3.9 Hz, 4H), 4.03-3.90 (m, 8H), 3.42 (dd, *J* = 12.9, 6.6 Hz, 4H), 1.97 (dt, *J* = 14.3, 7.1 Hz, 6H), 1.71 (dd, *J* = 12.0, 5.9 Hz, 2H), 1.61-0.85 (m, 84H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.76, 165.01, 164.65, 163.01, 153.36, 149.20, 139.16, 136.80, 131.92, 124.97, 123.65, 123.51, 121.52, 114.51, 112.64, 72.44, 71.58, 40.16, 39.62, 38.97, 33.81, 30.77, 29.61 29.55, 29.48, 29.43, 29.14, 29.09, 29.02, 28.94, 27.17, 24.10, 23.06, 14.10, 14.06. ESI-MS, *m/z* calcd for $[C_{80}H_{128}N_6O_{10} + H]^+$ 1333.9792; found: 1333.9747.

Multiple-hydrogen-bonded polymer: Toluene (0.2 mL), monomer **1** (50 mg, 0.036 mmol) and Grubbs' ruthenium catalyst (2nd generation, 3 mg) were charged into a sealed Schlenk-type tube equipped with Kontes high-vacuum valves in the drybox. The tube was then placed into a liquid nitrogen bath and was then connected to the vacuum line for a while. The tube was then placed into an oil bath preheated at the prescribed temperature (55 °C) and the mixture was stirred for prescribed time (24 h). During the reaction, the mixture was placed into a liquid nitrogen bath to remove ethylene from the reaction medium twice by opening the valve connected to the vacuum line and then placed into the oil bath to continue the reaction. An additional 1.7 mg of Grubbs' ruthenium catalyst in toluene (0.1 mL) was added after 24 h. The reaction lasted for a total of 48 h. The polymerization was quenched by adding ethyl vinyl ether in excess amount. The reaction mixture was then stirred for 1 h for completion. The solvent was removed by evaporation, the residue was dissolved in a minimum amount of chloroform and precipitated in hot ethanol. The hoariness precipitate was collected by filtration. Separation by PTLC (chloroform/methanol, 15:1) provide polymer MHP (**Scheme-II**).



Scheme-I: Synthetic route for oligoamide monomer 1



Scheme-II: Synthetic route for polymer MHP

RESULTS AND DISCUSSION

Acyclic diene metathesis polymerization: Acyclic diene metathesis polymerization of diene **1** was performed in dry toluene at atmospheric pressure. The reaction was monitored by ^{1}H NMR. The ^{1}H NMR spectra of Run 1 (Table-1) show distinct changes relative to their respective monomers. The formation of product is marked by the appearance of a resonance at 5.31 ppm, indicating the formation of the vinylene bond. The conversion was determined by integration of the olefinic signals at 4.94 and 5.31 ppm for monomer and polymer, respectively[9]. Unfortunately, initial attempts to polymerize **1** using the first-generation and the second-generation Grubbs' ruthenium

TABLE-1
ADMET POLYMERIZATION OF MONOMER **1**[a]

Run	Cat.(equiv)[b]	DP (NMR)	DP (GPC)[c]	Conv. (%)
1	1_{st}(10)	8	4	75
2	1_{st}(15)	5	5	75
3	2_{nd}(10)	8	5	80
4	2_{nd}(15)	5	5	80
5	2_{nd}(10)[d]	[e]	14	n.c[f]
6	2_{nd}(10)	[e]	16	n.c[f]

[a]Condition: initial monomer concentration: 180 mM; time: 48 h; temperature: 55 °C; [b]Molar ratio based on monomer/R_u; [c]Determined by GPC in THF *versus* polystyrene standards; [d]Postpolymerization using oligomer (DP = 5) as reactant; [e]Not determined due to absence of terminal double bonds signals; [f]Near-quantitative conversion of monomer to polymer

catalyst in toluene at atmosphere pressure did not yield polymer with high degree of polymerization (DP) (Table-1, Run 1-Run 4).

In order to improve the efficiency of the acyclic diene metathesis polymerization, two approaches have been used in the literature[10]. The first approach is the continuous removal of ethylene from the reaction system. This can be achieved by placing the reaction system into reduced pressure. (Table-1, Run 6). The second approach is postpolymerization (Table-1, Run 5). Postpolymerization was carried out with 48 mg of MHP ($DP_{NMR} = 5$) and 4.2 mg of Grubbs 2_{nd} catalyst in 0.2 mL of toluene at reduced pressure. The reaction lasted for a total of 24 h, during which time vacuum was applied twice to remove ethylene from the system. During the reaction, the viscosity of the reaction mixture changes, turning only after 8 h and highly viscous after 20 h, so stirring became difficult. This is due to partial loss of solvent as well as to the formation of polymers with higher degree of polymerization (DP) value. The degree of polymerization detected by gel permeation chromatography shows the increase of molecular weight. The ^{1}H NMR spectrum of Run 6 (Fig. 2) show the disappear of terminal vinyl signals, indicating the conversion of almost all terminal vinyl. However Run 6 with a Mn 15000 g/mol gel permeation chromatography showed a DP 12, supporting the formation of cyclic acyclic diene metathesis polymerization products[11].

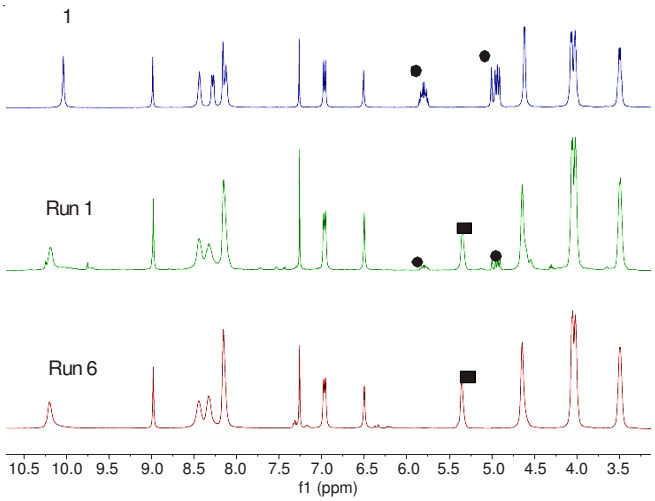


Fig. 2. ^{1}H NMR spectra of comparison of monomer **1**, polymer MHP (Run 1, Run 6)

Morphology of polymer MHP: The hydrogen-bonding-assisted assembled behaviour of polymer MHP was investigated by SEM technique. The SEM images of MHP (Fig. 3) in chloroform showed the polymer stacked into spherical structure probably due to its intermolecular and intramolecular association interactions induced by self-complementary multiple hydrogen bonding. It is evident that the high propensity of self-assemblies should result from their high association affinity of the binding units in backbone of polymer MHP.

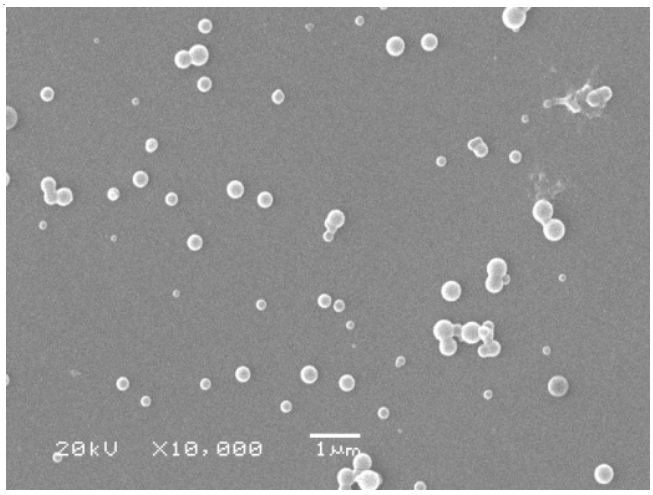


Fig. 3. SEM images of polymer MHP

Conclusion

In conclusion, the multiple hydrogen-bonded unit containing polymer was synthesized by using acyclic diene metathesis polymerization of oligoamide monomer **1** with Grubbs-type olefin metathesis catalysts. We have successfully increased degree of polymerization of MHP by placing reaction system into reduced pressure and postpolymerizaation. Surface morphology revealed by SEM image indicated that polymer MHP associated into spherical assemblies induced by self-complementary hydrogen-bonding.

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